

Gibbs-Jaynes Entropy Versus Relative Entropy

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Abstract

The maximum entropy formalism developed by Jaynes determines the relevant ensemble in nonequilibrium statistical mechanics by maximising the entropy functional subject to the constraints imposed by the available information. We present an alternative derivation of the relevant ensemble based on the Kullback-Leibler divergence from equilibrium. If the equilibrium ensemble is already known, then calculation of the relevant ensemble is considerably simplified. The constraints must be chosen with care in order to avoid contradictions between the two alternative derivations. The relative entropy functional measures how much a distribution departs from equilibrium. Therefore, it provides a distinct approach to the calculation of statistical ensembles that might be applicable to situations in which the formalism presented by Jaynes performs poorly (such as non-ergodic dynamical systems).

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INTRODUCTION

Edwin T. Jaynes wrote a beautiful article in 1957 [1] advocating a reinterpretation of statistical mechanics in light of Shannon’s mathematical theory of communication [2]. Instead of working with ensembles of systems, Jaynes posed the problem in the following terms: suppose we know the expected values of a set of functions F_1, \dots, F_k of the microscopic state z of a system, what is the best estimate for the average value of some other function $G(z)$? Without access to z , which is never available in the lab, the best that can be done is to pick a probability distribution $\rho(z)$ over the states and then calculate the expected value of G as $\text{Tr}[\rho G]$. But then we encounter the problem of which distribution ρ to choose, because the average values $\langle F_1 \rangle, \dots, \langle F_k \rangle$ do not provide enough information to determine ρ uniquely. We need an additional criterion. Therefore, argued Jaynes, one should use the distribution that maximises the Shannon entropy functional

$$H[\rho] \equiv - \sum_i \rho(z_i) \ln(\rho(z_i)), \quad (1)$$

subject to the constraints imposed by the information available. Any other distribution would imply an unjustified bias in the probabilities.

Shannon’s H functional applies only to discrete distributions, but the Gibbs-Jaynes entropy functional S is analogous to H for continuous sets of states, as in the case of points in phase space [3].

$$S[\rho] \equiv -k_B \int_{\Gamma} \rho(z) \ln \left(\frac{\rho(z)}{m(z)} \right) dz = -k_B \text{Tr} \left[\rho \ln \left(\frac{\rho}{m} \right) \right]. \quad (2)$$

In classical Hamiltonian dynamics, the measure $m(z)$ turns out to be h^{-3N} (N is the number of particles and h is Planck’s constant). Γ stands for the whole phase space and k_B for Boltzmann’s constant.

Jaynes’s maximum entropy formalism allows us not only to derive equilibrium statistical mechanics from the point of view of statistical inference, but also to select probability distributions in more general situations, when the expected values of several arbitrary phase functions have been established, even if they are not dynamical invariants. Working out such distributions constitutes the key step for projection operator techniques in the theory of transport processes [4–6].

Recent developments in nonequilibrium statistical mechanics [7–16] have borrowed an-

other tool from information theory known as the Kullback-Leibler divergence [17],

$$D(\rho\|\rho') \equiv \int_{\Gamma} \rho(z) \ln \left(\frac{\rho(z)}{\rho'(z)} \right) dz, \quad (3)$$

which measures how “different” ρ is from ρ' . A well-known result in information theory states that $D(\rho\|\rho') \geq 0$, with equality holding only when $\rho(z) = \rho'(z)$ almost everywhere.

When an equilibrium ensemble is used as the reference distribution, $\rho' = \rho^{eq}$, there is a simple connection between the Gibbs-Jaynes entropy (2) and the *relative entropy*, defined here as

$$\Delta S[\rho] \equiv -k_B D(\rho\|\rho^{eq}). \quad (4)$$

The link can easily be established the moment we realise that the equilibrium ensemble is a stationary solution of Liouville’s equation,

$$\frac{\partial \rho^{eq}}{\partial t} = 0, \quad (5)$$

and that ρ^{eq} must therefore be a function of the dynamical invariants only. Let $I(z)$ stand for the invariants for the microstate z , such as the energy, the linear momentum, and so forth. We then know that $\rho^{eq}(z)$ is some function $\Phi(I(z))$. The integral of ρ^{eq} over all the states that satisfy $I(z) = i$ should equal the probability $P(i)$ of finding the system in a state compatible with these values of the invariants.

$$\text{Tr} [\rho^{eq} \delta(I - i)] = \Phi(i) \text{Tr} [\delta(I - i)] = P(i), \quad (6)$$

where δ is the Dirac delta function. Solving for Φ , we end up with

$$\Phi(i) = \frac{P(i)}{\text{Tr} [\delta(I - i)]}, \quad (7)$$

which means that

$$\rho^{eq}(z) = \frac{P(I(z))}{h^{3N} \Omega(I(z))}. \quad (8)$$

The function $\Omega(i)$ in the denominator may be thought of as the “number of microstates” that satisfy $I(z) = i$,

$$\Omega(i) = \int_{\Gamma} h^{-3N} \delta(I(z) - i) dz. \quad (9)$$

When the expression for the equilibrium distribution (8) is substituted into the definition of the relative entropy (4), we find

$$\Delta S[\rho] = -k_B \int_{\Gamma} \rho(z) \ln \left(\frac{h^{3N} \rho(z)}{\frac{P(I(z))}{\Omega(I(z))}} \right) dz \quad (10)$$

$$\begin{aligned}
&= -k_B \int_{\Gamma} \rho(z) \ln \left(h^{3N} \rho(z) \right) dz + k_B \int_{\Gamma} \rho(z) \ln \left(\frac{P(I(z))}{\Omega(I(z))} \right) dz \\
&= S[\rho] + k_B \int \text{Tr} [\rho \delta(I - i)] \ln \left(\frac{P(i)}{\Omega(i)} \right) di,
\end{aligned}$$

(the latter integral is extended over all the values of i). Hence maximising the relative entropy functional ΔS is equivalent to maximising the Gibbs-Jaynes functional S *as long as this last integral is constant for the distributions allowed by the constraints*. A reasonable way to meet this condition requires

$$\text{Tr} [\rho \delta(I - i)] = P(i). \quad (11)$$

In other words, the agreement between both maximisation strategies is based on the assumption that the unknown distribution generates the same probability distribution over the dynamical invariants as the equilibrium ensemble. If equation (11) is conceded then, given the probability distribution at equilibrium, we can follow two different paths to calculate the least biased distribution compatible with our information about the system.

An anonymous reviewer pointed out that condition (11) could be relaxed when ρ^{eq} designates the canonical ensemble (36), for then we can simply assume that the expected energy calculated with ρ leads to the same result as when it is calculated with ρ^{eq} and then prove that the final integral in equation (10) becomes independent of ρ .

$$-k_B \int_{\Gamma} \rho(z) \ln \left(h^{3N} \rho^{eq}(z) \right) dz = -k_B \int_{\Gamma} \rho^{eq}(z) \ln \left(h^{3N} \rho^{eq}(z) \right) dz = S[\rho^{eq}] \quad (12)$$

Hence, in the canonical case condition (11) may be relaxed to

$$\text{Tr}[\rho I] = \text{Tr}[\rho^{eq} I] \quad (13)$$

Similarly, for a microcanonical ρ^{eq} , it is enough to require that ρ vanishes whenever ρ^{eq} does.

GENERALISED CANONICAL PROBABILITY DISTRIBUTION

Let us illustrate the two alternative maximisation routes by working out the classic example of the probability distribution for a system in contact with a heat bath at temperature T . We shall start with the Gibbs-Jaynes functional and introduce two habitual assumptions. First, we will imagine that the system and the reservoir have been isolated from the rest of the universe, and second, we will disregard the interaction energy between them, which we

assume is very small compared with their internal energies, so that the Hamiltonian, which remains constant, may be expressed as a sum of two terms,

$$H(z) = H_S(z_S) + H_R(z_R), \quad (14)$$

the former corresponding to our system, and the latter to the reservoir.

A typical setup might also include the measured values of several macroscopic variables, such as concentrations or hydrodynamic velocity fields [5]. We denote these values f_1, \dots, f_k and equate them to the averages for the corresponding functions $\langle F_1 \rangle, \dots, \langle F_k \rangle$, of the microstate z_S

$$f_i = \text{Tr} [\rho F_i], \quad (15)$$

where ρ is the unknown distribution. Given the one-to-one correspondence between the equilibrium temperature T and the total internal energy, we include an additional constraint for the expected value of $H(z)$,

$$E = \text{Tr} [\rho H], \quad (16)$$

although we do not yet know the actual number represented by E . Finally, we must ensure that ρ is properly normalised,

$$\text{Tr} [\rho] = 1. \quad (17)$$

Gibbs-Jaynes entropy functional

We now wish to find the distribution that maximises the entropy functional subject to all the constraints (15)-(17). Following the standard method of Lagrange multipliers, we add constraint terms to the Gibbs-Jaynes functional (2) to obtain

$$\begin{aligned} C[\rho] = & -k_B \text{Tr} [\rho \ln (h^{3N} \rho)] - k_B \sum_{i=1}^k \lambda_i (\text{Tr} [\rho F_i] - f_i) \\ & - k_B \beta (\text{Tr} [\rho H] - E) - k_B \mu (\text{Tr} [\rho] - 1). \end{aligned} \quad (18)$$

The λ_i , β and μ are all Lagrange multipliers. The functional derivative of C with respect to ρ should vanish for the least biased distribution, frequently called the *relevant* distribution, $\bar{\rho}$,

$$\left. \frac{\delta C}{\delta \rho} \right|_{\rho=\bar{\rho}} = 0, \quad (19)$$

and this equation leads us to

$$\bar{\rho} = h^{-3N} e^{-\sum_{i=1}^k \lambda_i F_i - \beta H - \mu - 1}. \quad (20)$$

Substitution of $\bar{\rho}$ into the constraints should allow us, in principle, to calculate the Lagrange multipliers. Equation (17), for example, determines the value of μ . When combined with (20), we find that

$$e^{-\mu-1} = \frac{1}{\text{Tr} \left[h^{-3N} e^{-\sum_{i=1}^k \lambda_i F_i - \beta H} \right]} = \frac{1}{Z}, \quad (21)$$

so our probability distribution becomes

$$\bar{\rho}(z) = \frac{1}{h^{3N} Z} e^{-\sum_{i=1}^k \lambda_i F_i(z_S) - \beta H(z)}. \quad (22)$$

Equation (14) implies that the partition function Z factors into the product of an integral over z_S and another over z_R . We will refer to these factors as Z_S and Z_R .

$$\begin{aligned} Z &= \left(\int_{\Gamma_S} h^{-3N_S} e^{-\sum_{i=1}^k \lambda_i F_i(z_S) - \beta H_S(z_S)} dz_S \right) \left(\int_{\Gamma_R} h^{-3N_R} e^{-\beta H_R(z_R)} dz_R \right) \\ &= Z_S Z_R, \end{aligned} \quad (23)$$

where N_S and N_R are the number of particles in the system and reservoir, respectively.

We define the entropy $S(E, f_1, \dots, f_k)$ as the maximum value of the Gibbs-Jaynes entropy functional. Inserting the expression for $\bar{\rho}$ into (2) reveals the following link between the partition function and the entropy:

$$S(E, f_1, \dots, f_k) \equiv S[\bar{\rho}] = k_B \ln(Z) + k_B \sum_{i=1}^k \lambda_i f_i + k_B \beta E. \quad (24)$$

Factoring Z according to (23), the entropy separates neatly into two terms,

$$S(E, f_1, \dots, f_k) = k_B \left(\ln(Z_S) + \sum_{i=1}^k \lambda_i f_i + \beta E_S \right) + k_B (\ln(Z_R) + \beta E_R) \quad (25)$$

where E_S and E_R stand for the expected values of H_S and H_R . On the right of equation (25) we find the entropies of the system and reservoir considered separately. In other words, suppose we had isolated the system from the heat bath and had then calculated the entropies for both independently by maximising the Gibbs-Jaynes functional, with the same constraints on the average values of F_1, \dots, F_k and the normalisation of ρ , but changing the constraints on the expected energies to $\langle H_S \rangle_S = E_S$ for the system and $\langle H_R \rangle_R = E_R$ for

the bath, where E_S and E_R are the same values as in equation (25). Then the expressions for the entropies, S_S for the system and S_R for the reservoir, would read

$$\begin{aligned} S_S(f_1, \dots, f_k, E_S) &= k_B \left(\ln(Z_S) + \sum_{i=1}^k \lambda_i f_i + \beta_S E_S \right), \\ S_R(E_R) &= k_B (\ln(Z_R) + \beta_R E_R). \end{aligned} \quad (26)$$

We will show below that the sum $S_S + S_R$ equals S in (25) because

$$\beta_S = \beta_R = \beta. \quad (27)$$

The set of equations (25), (26) and (27) illustrates the well-known fact that entropy is an extensive quantity if the interaction between subsystems is small enough to be disregarded. The equality of the three Lagrange multipliers in (27) can be verified by comparing the average values calculated using (22) to the averages for the system and reservoir considered independently, noting that

$$\begin{aligned} \langle H_S \rangle_S &= \langle H_S \rangle = E_S, \\ \langle H_R \rangle_R &= \langle H_R \rangle = E_R. \end{aligned} \quad (28)$$

The Lagrange multiplier β_R is related to the temperature of the heat bath according to

$$\frac{1}{T} = \frac{\partial S_R}{\partial E_R} = k_B \beta_R. \quad (29)$$

Therefore, equation (27) shows that the temperatures of the system and the bath must equal the same value T for the relevant distribution, and

$$\beta = \frac{1}{k_B T}. \quad (30)$$

Equation (22) then becomes

$$\bar{\rho}(z) = \frac{1}{h^{3N} Z} e^{-\sum_{i=1}^k \lambda_i F_i(z_S) - \frac{1}{k_B T} H_S(z_S) - \frac{1}{k_B T} H_R(z_R)}. \quad (31)$$

To calculate the probability distribution for z_S , we can now integrate over the degrees of freedom of the reservoir, that is,

$$\bar{\rho}_S(z_S) = \int \bar{\rho}(z) dz_R. \quad (32)$$

The answer to our problem, known as the generalised canonical probability distribution [5], is the least biased probability distribution for a system at constant temperature T that also satisfies the constraints (15). Carrying out the integral (32), we obtain

$$\bar{\rho}_S(z_S) = \frac{e^{-\sum_{i=1}^k \lambda_i F_i(z_S) - \frac{1}{k_B T} H_S(z_S)}}{\text{Tr} \left[e^{-\sum_{i=1}^k \lambda_i F_i(z_S) - \frac{1}{k_B T} H_S(z_S)} \right]}, \quad (33)$$

where the trace should now be interpreted as an integration over z_S .

Relative entropy functional

Now consider the derivation of the generalised canonical distribution (33) from the relative entropy (4). In that case, we do not need to pay attention to the reservoir, so we maximise the functional ΔC , which includes the relative entropy and constraints (15) and (17).

$$\Delta C = -k_B \text{Tr} \left[\rho \ln \left(\frac{\rho}{\rho^{eq}} \right) \right] - k_B \sum_{i=1}^k \lambda_i (\text{Tr} [\rho F_i] - f_i) - k_B \mu (\text{Tr} [\rho] - 1). \quad (34)$$

As before, we calculate the functional derivative of ΔC with respect to ρ and find that

$$\bar{\rho} = \rho^{eq} e^{-\sum_{i=1}^k \lambda_i F_i - \mu - 1}. \quad (35)$$

The equilibrium distribution ρ^{eq} for a system at constant temperature is the well-known canonical ensemble,

$$\rho^{eq}(z_S) = \frac{e^{-\frac{1}{k_B T} H_S(z_S)}}{\text{Tr} \left[e^{-\frac{1}{k_B T} H_S(z_S)} \right]}. \quad (36)$$

By ensuring that $\bar{\rho}$ is normalised, we determine μ

$$e^{-\mu-1} = \frac{\text{Tr} \left[e^{-\frac{1}{k_B T} H_S(z_S)} \right]}{\text{Tr} \left[e^{-\sum_{i=1}^k \lambda_i F_i(z_S) - \frac{1}{k_B T} H_S(z_S)} \right]}. \quad (37)$$

And substituting (36) and (37) into (35), we recover the generalised canonical probability distribution (33).

Jaynes's maximum entropy formalism guided us to the desired solution, but the path we had to follow was not as direct as the relative entropy route. Furthermore, in the former derivation, we found ourselves describing the effect of the reservoir in terms of the total energy $E = E_S + E_R$. But knowledge of the energy in the reservoir, E_R , clearly has no

bearing on our problem because heat baths are characterised by their temperature, not their internal energy, and it is a good thing that E_R eventually drops out of the equations. Therefore, if we already know the equilibrium ensemble, perhaps it is easier to derive the relevant distribution from the relative entropy functional. Nevertheless, the functional form of equation (33) could have been inferred from the Gibbs-Jaynes entropy (2) by a simpler procedure that does not contemplate the reservoir. The idea is to use the constraints for the average values f_i (15), normalisation (17) and an extra constraint for the expected value of the unknown energy E_S . The maximum entropy formalism then leads to an expression analogous to (33), but with an unknown coefficient before $H_S(z_S)$. All the extra work with the reservoir in the subsection on the Gibbs-Jaynes derivation was carried out to establish that the temperature in equation (33) was equal to the temperature of the reservoir T (note that we have not assumed thermal equilibrium between the reservoir and system of interest). When the same result was derived from the relative entropy functional (4) we did not have to do any of this extra work because the relevant information was already captured in the equilibrium distribution.

AN APPARENT PARADOX

The preceding discussion might give the impression that the relevant distribution may always be expressed as

$$\bar{\rho}(z) = \frac{\rho^{eq}(z)}{\mathcal{Z}} e^{\sum_i \lambda_i F_i(z)}, \quad (38)$$

where \mathcal{Z} stands for the appropriate normalisation factor. But this rule may lead to incorrect conclusions if applied carelessly. To see why, let us examine a slightly more general problem.

Whenever we are dealing with macroscopic systems in experiments, the exact number of atoms or molecules remains unknown. Let z_N represent the coordinates and momenta of a system of N particles. The probability distributions and functions will now depend on the dimensionality of phase space, so we will write them with a subindex N to emphasise this dependence. The Gibbs-Jaynes entropy functional (2) can be generalised to

$$S = -k_B \sum_N \int_{\Gamma_N} \rho_N(z_N) \ln \left(h^{3N} \rho_N(z_N) \right) dz_N, \quad (39)$$

and the constraints on the average values $\langle F_1 \rangle, \dots, \langle F_k \rangle$ now read

$$f_i = \sum_N \int_{\Gamma_N} \rho_N(z_N) F_{i,N}(z_N) dz_N, \quad (40)$$

where Γ_N represents the phase space for N particles. Similarly, the expression for the relative entropy turns into

$$\Delta S = -k_B \sum_N \int_{\Gamma_N} \rho_N(z_N) \ln \left(\frac{\rho_N(z_N)}{\rho_N^{eq}(z_N)} \right) dz_N. \quad (41)$$

The obvious generalisation of (38) must be

$$\bar{\rho}_N(z_N) = \frac{\rho_N^{eq}(z_N)}{\mathcal{Z}} e^{\sum_i \lambda_i F_{i,N}(z_N)}. \quad (42)$$

Note that $\rho_N(z_N)$ and $\rho_N^{eq}(z_N)$ represent joint probability densities for N and z_N , and are therefore not normalised to one, but rather

$$\int_{\Gamma_N} \rho_N(z_N) dz_N = \int_{\Gamma_N} \rho_N^{eq}(z_N) dz_N = P(N), \quad (43)$$

where $P(N)$ represents the probability of N particles in the system.

Imagine an isolated system for which we know the probability distribution $P(E, N)$ for the total energy E and number of particles N . Both E and N are dynamical invariants, and so is the probability $P(E, N)$. Hence we should find the same probability for E and N at equilibrium.

$$\begin{aligned} P(E, N) &= \int_{\Gamma_N} \rho_N(z_N) \delta(H_N(z_N) - E) dz_N \\ &= \int_{\Gamma_N} \rho_N^{eq}(z_N) \delta(H_N(z_N) - E) dz_N. \end{aligned} \quad (44)$$

If we use Lagrange's method to maximise (39) subject to (40) and (44), we derive the set of relevant distributions

$$\bar{\rho}_N(z_N) = P(H_N(z_N), N) \frac{e^{\sum_i \lambda_i F_{i,N}(z_N)}}{\int_{\Gamma_N} e^{\sum_i \lambda_i F_{i,N}(z'_N)} \delta(H_N(z'_N) - H_N(z_N)) dz'_N}. \quad (45)$$

But in general these functions are formally different from our previous expression for $\bar{\rho}_N$ (42).

The disagreement between the two methods dissolves when we carry out the operations carefully. It might seem at first that there is no need to include the constraint (44) when we maximise the functional for the relative entropy, because all the relevant information about $P(E, N)$ should already be included in the equilibrium distribution. However, we do in fact have to specify that the distribution we are looking for must lead to the same value as the equilibrium distribution when both are integrated over a given constant energy manifold.

When using the relative entropy (41), the correct functional to maximise is thus

$$\begin{aligned} \Delta C = \Delta S - k_B \sum_i \lambda_i \left(\sum_N \int_{\Gamma_N} \rho_N(z_N) F_{i,N}(z_N) dz_N - f_i \right) \\ - k_B \sum_N \int_0^\infty \mu(E, N) \left(\int_{\Gamma_N} \rho_N(z_N) \delta(H_N(z_N) - E) dz_N - P(E, N) \right) dE. \end{aligned} \quad (46)$$

The last term above includes a Lagrange multiplier μ for each pair of E and N , as required by equation (44). Once again, we equate the derivatives of ΔC to zero and solve for the relevant distribution to find

$$\bar{\rho}_N(z_N) = \rho_N^{eq}(z_N) e^{-\mu(H_N(z_N), N) - 1 - \sum_i \lambda_i F_{i,N}(z_N)}. \quad (47)$$

This distribution can be identified with (42) as long as \mathcal{Z} is interpreted as a function of E and N . In other words, if we define

$$\mathcal{Z}(E, N) = e^{\mu(E, N) + 1}, \quad (48)$$

then we can simply insert (47) into (44) and solve for \mathcal{Z} , to determine

$$\mathcal{Z}(E, N) = \frac{\int_{\Gamma_N} \rho_N^{eq}(z_N) e^{-\sum_i \lambda_i F_{i,N}(z_N)} \delta(H_N(z_N) - E) dz_N}{P(E, N)}. \quad (49)$$

Recalling the expression for the equilibrium distribution (8),

$$\rho_N^{eq}(z_N) = \frac{P(H_N(z_N), N)}{h^{3N} \Omega_N(H_N(z_N))}, \quad (50)$$

equations (48)-(50) can be used to convert (47) into (45), so the two methods once again lead to the same result, as they should.

PRELIMINARY RESULTS CONCERNING APPLICATIONS

In the literature, relative entropy has been applied mainly to the calculation of nonequilibrium free energy differences [7, 8, 16] and dissipated work [9]. In that context, ρ and ρ^{eq} are both distributions that can be realised physically, such as the equilibrium ensembles of a given Hamiltonian. By contrast, in the present paper we have used the relative entropy functional to determine *relevant distributions*, which need not be realised physically, because they represent the least-biased distribution that is consistent with the information available.

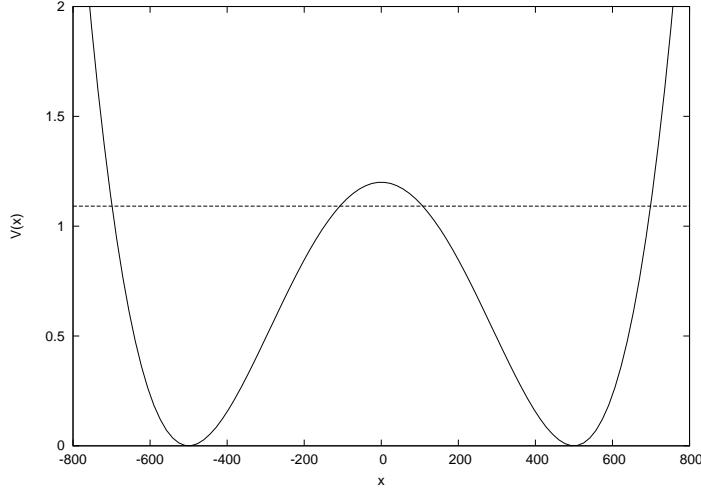


FIG. 1. Double-well potential confining $N = 100$ Lennard-Jones particles. The dashed line marks the average energy per particle E/N .

Within the theory of Mori-Zwanzig transport processes, relevant distributions have become a crucial tool to derive generalised transport equations [4–6]. Consider the one-dimensional isolated double-well potential drawn in figure 1, which confines one hundred particles that interact with each other through the Lennard-Jones potential. Let the relevant variable $F(z)$ represent the number of particles on the right,

$$F(z) = \sum_{i=1}^N \theta(q_i), \quad (51)$$

where θ is the Heaviside step function and q_i the position of particle i . The Mori-Zwanzig theory of nonequilibrium transport allows us to write exact transport equations for the average value of any phase function [5]. In particular, for the relevant variable in (51), the theory produces the following transport equation for the average value $\langle F \rangle = f$,

$$\frac{\partial f}{\partial t} = -v(f) + \int_0^t K(t, s) ds. \quad (52)$$

The first term on the right is known as the organized drift, v , while K is called the after-effect function. Here we will concentrate only on the organized drift, defined as

$$v(f) = \text{Tr} [\bar{\rho} \hat{\mathbf{L}} F] = \text{Tr} \left[\bar{\rho} \sum_{i=1}^N \delta(q_i) \frac{p_i}{m_i} \right], \quad (53)$$

as a first crude approximation to the time rate of change for f . That is to say, we are assuming that $K(t, s) \approx 0$. In (53) we have applied the Liouville operator $\hat{\mathbf{L}}$ to F to

calculate how v is related to the momenta p_i and masses m_i of the particles.

$$\hat{\mathbf{L}}F = \{H, F\} = \sum_{i=1}^N \delta(q_i) \frac{p_i}{m_i} \quad (54)$$

If we follow Jaynes's maximum entropy route to determine the relevant distribution $\bar{\rho}$ for f equal to some value N_R , then we get

$$\bar{\rho}(z) = \frac{\delta(H(z) - E) e^{-\lambda_{N_R} F(z)}}{\text{Tr} [\delta(H(z) - E) e^{-\lambda_{N_R} F(z)}]}, \quad (55)$$

with the Lagrange multiplier λ_{N_R} chosen to satisfy the constraint on the average value of F . When we insert (55) in (53) and integrate, the organised drift vanishes because it is the integral of an odd function, due to the presence of the momenta p_i .

$$v(f) = 0. \quad (56)$$

Surprisingly, in many cases this conclusion (56) is incorrect. Suppose we choose an initial state with all the particles on the left. If the average energy per particle E/N lies below the height of the potential barrier, then the system can never reach a state with all the particles on the right, simply because there is not enough energy to get them all over the barrier. Note, though, that when we switch the signs of all the coordinates in our initial state we create a new inaccessible state with the same total energy as before. In other words, the system is not ergodic for some values of the energy E , and so it does not explore the complete $H(z) = E$ surface in phase space.

Let ρ^{ref} designate the final stationary distribution reached by the system, to distinguish it from the microcanonical ρ^{eq} implied by the maximum entropy approach. Calculating the relevant distribution from the relative entropy functional (4), the expression for the organised drift becomes

$$v(N_R) = \frac{\text{Tr} [\rho^{ref} e^{-\lambda_{N_R} F} \hat{\mathbf{L}}F]}{\text{Tr} [\rho^{ref} e^{-\lambda_{N_R} F}]}. \quad (57)$$

Even though ρ^{ref} is unknown, we can sample it by means of a molecular dynamics simulation. After the simulation run, the system has traversed a set of points $\{z_j\}$, so we estimate $v(N_R)$ with

$$v(N_R) \approx \frac{\sum_j e^{\lambda_{N_R} F(z_j)} \hat{\mathbf{L}}F(z_j)}{\sum_j e^{\lambda_{N_R} F(z_j)}}. \quad (58)$$

Figure 2 represents the number of particles on the right of the double-well potential in figure 1 as a function of time. We started the simulation with all the particles on the left

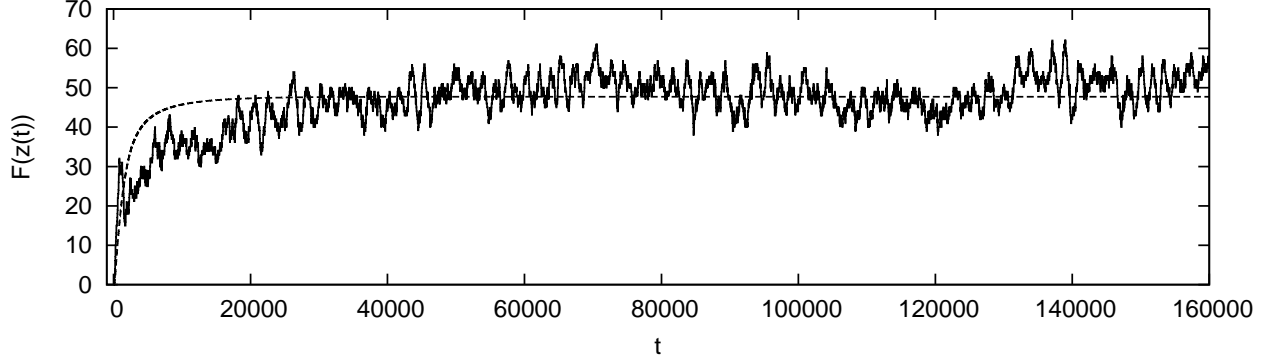


FIG. 2. Number of particles with a positive coordinate value versus time for a system of $N = 100$ Lennard-Jones particles initially to the left of the potential barrier in figure 1. A classic Runge-Kutta fourth order algorithm with time step equal to 10^{-4} was used to integrate the equations of motion. The total energy remained constant to four significant figures. Numerical integration with the organised drift from figure 3 allowed us to estimate the average value of F as a function of time (dashed line).

and an average energy per particle E/N below the height of the potential barrier. The average kinetic temperature calculated over the whole run ($1.6 \cdot 10^9$ time steps) equals $T_{kin}/k_B = 1.2 \pm 0.1$ (mean \pm standard deviation). When the particles on either side of the barrier were considered separately, the average kinetic temperature remained the same, but the standard deviation doubled on the right of the well $T_{kin,R}/k_B = 1.2 \pm 0.2$.

Figure 3 shows the organised drift calculated with (58) as a function of the average number of particles N_R to the right of the potential barrier. Numerical integration of equation (52) by setting $K(t, s) = 0$ generated the dashed line shown in figure 2, which agrees qualitatively with the general trend of the simulation. The deviations observed are not very surprising, considering that we have completely neglected the after-effect function.

In summary, even though we have neglected the memory effects in the equation for the organised drift (53) calculated with the relative entropy (as opposed to the Gibbs-Jaynes entropy method), we have achieved a very good description of the transport over the energy barrier. The results are especially interesting because the dynamical evolution took place under non-ergodic conditions.

The method presented here could also be applied in principle to the numerical calculation of the integral of $K(t, s)$ in (52), but this would involve a much greater computational cost,

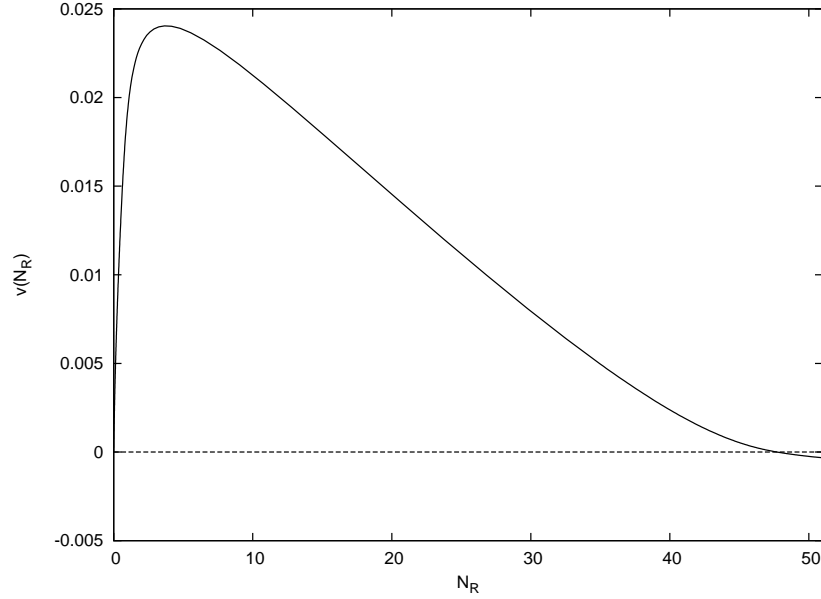


FIG. 3. Organised drift versus average number of particles to the right of the potential barrier, N_R , calculated with equation (58).

so we have deferred these calculations to future research.

CONCLUSIONS

In the context of the maximum entropy formalism, relative entropy (4) has pleasant features. Its maximum value, $\Delta S = 0$, obviously corresponds to equilibrium, and it enables us to calculate the relevant distribution with less effort. Furthermore, the relevant distribution turns into the equilibrium ensemble when the Lagrange multipliers λ_i vanish. With expressions like (35) or (47) this fact lies in plain sight.

Given the equilibrium ensemble ρ^{eq} and a set of constraints on average values, $\langle F_i \rangle = f_i$, the relevant distribution can be calculated immediately by following these rules: first, write

$$\bar{\rho} = \frac{\rho^{eq}}{Z} e^{-\sum_i \lambda_i F_i}. \quad (59)$$

Then ensure that $\bar{\rho}$ is normalised by writing

$$\text{Tr} [\bar{\rho}] = 1 \quad (60)$$

and solving for the partition function Z . Finally, the λ_i Lagrange multipliers can be calculated, at least in principle, by inserting $\bar{\rho}$ into the constraints on the average values, $\langle F_i \rangle = f_i$,

and solving for the λ_i .

The constraints for isolated systems must be considered carefully, because knowledge of the equilibrium ensemble reveals the probability distribution $P(i)$ over the whole set of values of the dynamical invariants through

$$\text{Tr} [\rho^{eq} \delta(I - i)] = P(i). \quad (61)$$

This information must be taken into account, so in this case we write

$$\bar{\rho} = \frac{\rho^{eq}}{\mathcal{Z}(i)} e^{-\sum_j \lambda_j F_j}. \quad (62)$$

Then we ensure that $\bar{\rho}$ is normalised by writing

$$\text{Tr} [\bar{\rho} \delta(I - i)] = P(i), \quad (63)$$

and solving for $\mathcal{Z}(i)$. The relevant ensemble can then be used in conjunction with the other constraints to find the value of the unknown Lagrange multipliers.

The relative entropy method relies on our knowledge of the equilibrium ensemble, and it provides no clues regarding how to calculate this probability distribution, unlike Jaynes's method. However, this might also be interpreted as a virtue. When the system has concealed dynamical invariants which have not been taken into account, maximising the Gibbs-Jaynes entropy will not generally reproduce the measured average values faithfully. This would signal the existence of missing information. By contrast, if the equilibrium ensemble has been determined by other means or if we are able to sample it effectively (with molecular dynamics, for example), then we have simultaneously determined the probability distribution for all the dynamical invariants. We may then simply write the relevant distribution in terms of the equilibrium ensemble and, in principle, use it to calculate nonequilibrium quantities like the coarse-grained free energy or Green-Kubo transport coefficients [5].

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